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## On the Basicity of Carboranylphosphines

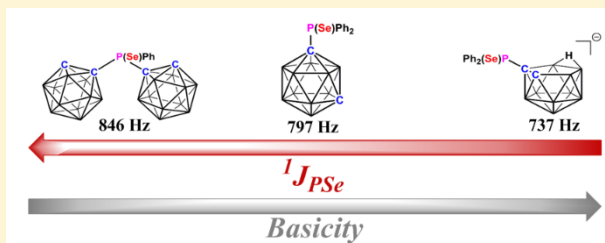
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**ABSTRACT:** Three new carboranylphosphines, [1-(1'-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>], [1-(1'-7'-PPh<sub>2</sub>-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] and [1-{PPh-(1'-*closo*-1',2'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] have been prepared and, from a combination of these and literature compounds, eight new carboranylphosphine selenides were

subsequently synthesized. The relative basicities of the carboranylphosphines were established by (i) measurement of the <sup>1</sup>J<sub>PSe</sub> NMR coupling constant of the selenide and (ii) calculation of the proton affinity of the phosphine, in an attempt to establish which of several factors are the most important in controlling basicity. It is found that the basicity of carboranylphosphines is significantly influenced by the nature of other substituents on the P atom, the nature of the carborane cage vertex (C or B) to which the P atom is attached and the charge on the carboranylphosphine. In contrast, the basicity of carboranylphosphines appears to be relatively insensitive to the nature of other substituents on the carborane cage, the isomeric form of the carborane and whether the cage is *closo* or *nido* (insofar as that does not alter the charge on the cluster). Such information is likely to be of significant importance in optimizing future applications of carboranylphosphines, e.g. as components of Frustrated Lewis Pairs.



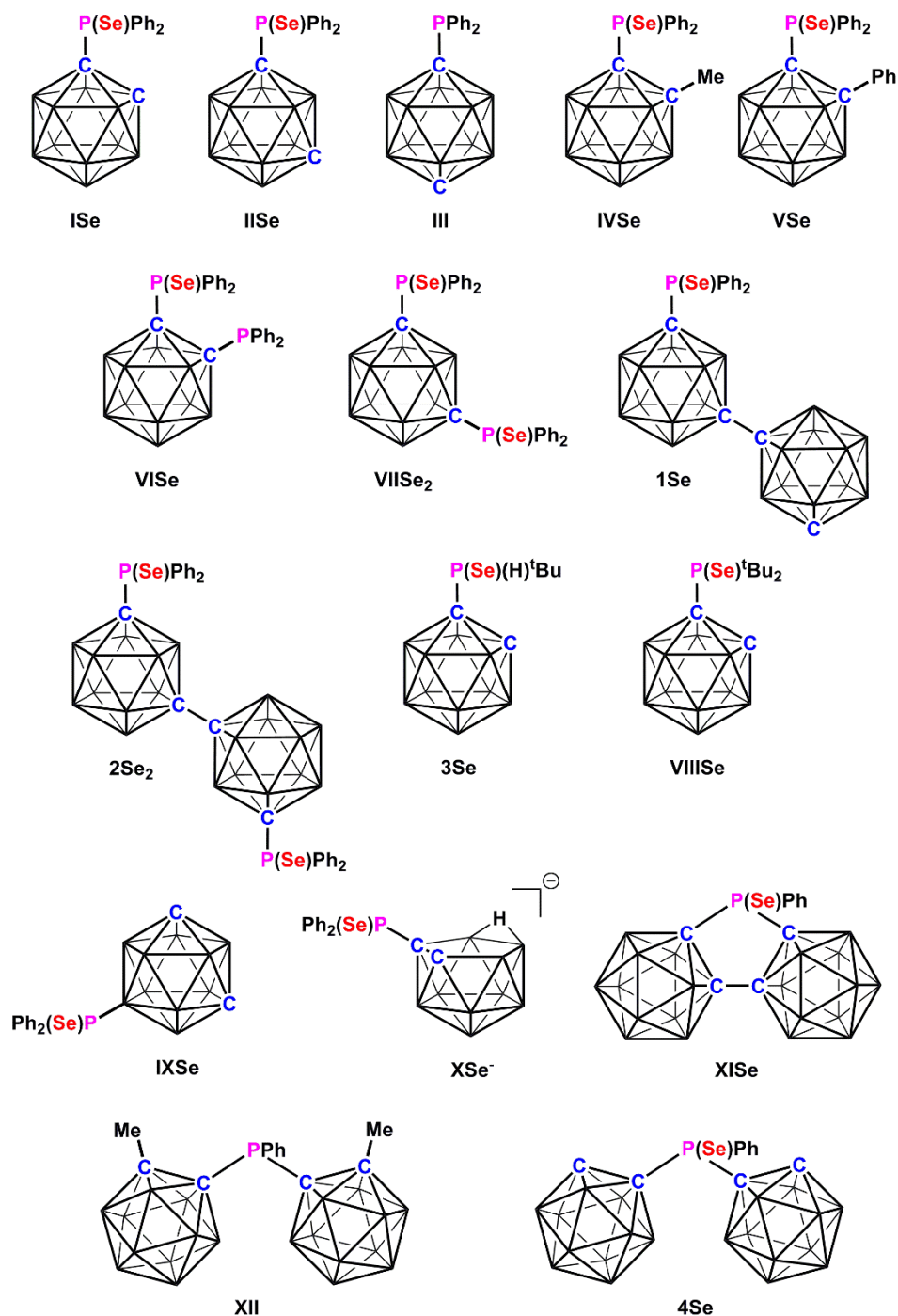
## ■ INTRODUCTION

The first carboranylphosphine, [1,2-(PPh<sub>2</sub>)<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (**VI**),<sup>1e</sup> was reported in the fifth of a landmark series of ten contiguous papers published in *Inorganic Chemistry* in 1963 describing the icosahedral carboranes [*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] and [*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] and their early derivatives.<sup>1</sup> Since then carboranylphosphines have been extensively studied, in large measure because incorporating a carborane unit into a phosphine affords a species which is usually readily synthesised, relatively stable and considerably sterically- and electronically-tuneable, thus facilitating an extensive chemistry including coordination chemistry.<sup>2</sup>

Our interest in carboranylphosphines stems from our recent report of the use of such species as the Lewis base component of Frustrated Lewis Pairs (FLPs).<sup>3</sup> We were attracted to carboranylphosphines for this application for the reasons given above, in particular the possibility of almost limitless tuneability of the Lewis base strength that a carborane scaffold potentially affords. Control of the acid and/or base strength of Lewis acid/Lewis base components of FLPs is important in optimizing the use of FLPs in catalysis,<sup>4</sup> and therefore it is essential that, for carboranylphosphines, we understand the factors that influence their Lewis base strength. It is now well established that a carborane substituted at *C* acts as an electron-withdrawing group (EWG) while when substituted at *B* distant from *C* it is an electron-donating group (EDG),<sup>5</sup> but there is much more variability inherent in carboranes. The carborane cage can exist in differing isomeric forms, can be deboronated to afford a nido anion, and can be substituted at both *B* and *C* vertices with a wide variety of groups. It is thus of interest to explore how these variations will be reflected in the basicity of an appended phosphine.

In this contribution, we explore the relative basicities of a range of both new and literature-reported carboranylphosphines through their derivatisation to the corresponding selenide, making use of the well-established inverse correlation between base strength and <sup>1</sup>*J* <sup>31</sup>P-<sup>77</sup>Se NMR coupling constant.<sup>6</sup> We also describe calculations on selected carboranylphosphines to estimate proton affinities (PA) and we show how these can serve as a surrogate in rank-ordering phosphine basicity in cases where the selenide is unobtainable.

**Chart 1** summarises the phosphines or their selenides considered in this work. If the phosphine is a literature species it is denoted by a Roman numeral (**I**, **II**, **III**, etc) whereas if it is reported here for the first time an Arabic numeral is used (**1**, **2**, **3**, etc). Selenides are described by appending either **Se** or **Se<sub>2</sub>** to the appropriate phosphine numeral (**ISe**, **VISe<sub>2</sub>**, **3Se**, etc). All the selenides described in this paper are previously unreported with the exception of **ISe**,<sup>3</sup> **IVSe**,<sup>7</sup> **VSe**,<sup>7</sup> **VISe**,<sup>7</sup> **IXSe**<sup>3</sup> and **XISe**.<sup>8</sup>



**Chart 1.** The carboranylphosphines considered in this study and, if known, their selenides. Roman numerals denote phosphine reported previously. Arabic numerals denote phosphines reported here for the first time. Selenides denoted by appending Se or Se<sub>2</sub> to label. The selenides **IISe**, **VIISe<sub>2</sub>**, **1Se**, **2Se<sub>2</sub>**, **3Se**, **VIIISe**, **XSe<sup>-</sup>** and **4Se** are previously unreported.

## ■ EXPERIMENTAL SECTION

### Synthesis and Spectroscopic Characterization

Experiments were performed under dry, oxygen-free N<sub>2</sub> using standard Schlenk techniques, although subsequent manipulations were occasionally performed in the open laboratory. Solvents were freshly distilled under nitrogen from the appropriate drying agent [40–60 petroleum ether (petrol) and diethyl ether; sodium wire: CH<sub>2</sub>Cl<sub>2</sub> (DCM); calcium hydride] and were degassed (3×freeze-pump-thaw cycles) before use. Toluene and fluorobenzene were stored over 4 Å molecular sieves and degassed before use. Deuterated solvents for NMR spectroscopy [CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>CO] were stored over 4 Å molecular sieves prior to use with additional drying procedures for C<sub>6</sub>D<sub>6</sub> (distilled under N<sub>2</sub> from molten potassium). Preparative thin-layer chromatography (TLC) employed 20×20 cm<sup>2</sup> Kieselgel F<sub>254</sub> glass plates and column chromatography used 60 Å silica as the stationary phase. NMR spectra at 400.1 MHz (<sup>1</sup>H), 128.4 MHz (<sup>11</sup>B), 162.0 MHz (<sup>31</sup>P) and 76.4 MHz (<sup>77</sup>Se) were recorded on a Bruker AVIII-400 spectrometer at room temperature. Elemental analyses were conducted using an Exeter CE-440 elemental analyzer. Electron ionization mass spectrometry (EIMS) was carried out using a Finnigan MAT900XP-Trap mass spectrometer at the University of Edinburgh. Carboranylphosphines **VII**,<sup>9</sup> **VIII**,<sup>10</sup> and **XII**,<sup>11</sup> 1,1'-bis(*meta*-carborane)<sup>12c</sup> and the carboranylphosphine selenide **ISe**<sup>3</sup> were prepared according to the literature. Compound **II** was synthesized by the published procedure<sup>13</sup> but using stoichiometric amounts of reagent, affording a significantly enhanced yield. All other reagents were purchased from commercial sources (Sigma Aldrich, Fluorochem, Acros Organics, Katchem) and used without further purification.

#### [1-(1'-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (1)

1,1'-Bis(*meta*-carborane) (300 mg, 1.05 mmol) was dissolved in toluene (25 mL). The solution was cooled to 0 °C before <sup>n</sup>BuLi (0.85 mL of a 1.6 M solution in hexanes, 1.36 mmol) was added dropwise. The pale yellow suspension was stirred for 2 h at room temperature then cooled to 0 °C. ClPPh<sub>2</sub> (0.25 mL, 1.36 mmol) was added dropwise. The suspension turned from yellow to white and was stirred overnight at room temperature. Toluene (2×5 mL) was added to the reaction mixture and the soluble materials were filtered off and evaporated to a white solid. The product was purified by preparative TLC (30:70, DCM:petrol; R<sub>f</sub> = 0.65) and isolated as a white solid (136 mg, 28%). During purification, compound **2** was also isolated (47 mg, 7%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.78–7.73 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.49–7.43 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 2.91 (br s, 1H, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -1.1 to -5.9 (3B), -5.9 to -15.8 (17B). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 20.7 (s). EIMS: envelope centered on *m/z* 470.5 (M<sup>+</sup>).

#### [1-(1'-7'-PPh<sub>2</sub>-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (2)

Similarly, 1,1'-bis(*meta*-carborane) (300 mg, 1.05 mmol) in toluene (30 mL) at 0 °C was deprotonated with <sup>n</sup>BuLi (1.96 mL of a 1.6 M solution in hexanes, 3.14 mmol) before ClPPh<sub>2</sub> (0.58 mL, 3.14 mmol) was added. Products were extracted into toluene (2×5 mL), filtered and purified by preparative TLC (30:70, DCM:petrol; R<sub>f</sub> = 0.47), and isolated as white solids (compound **2**, 50 mg, 11%; compound **1**, 54 mg, 11%). Single crystals of **2** were grown from a concentrated solution of fluorobenzene layered with petrol at -20 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.65–7.61 (m, 8H, C<sub>6</sub>H<sub>5</sub>), 7.42–7.33 (m, 12H, C<sub>6</sub>H<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -1.2 to -6.3 (4B), -6.3 to -15.8 (16B). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 20.8 (s). EIMS: envelope centered on *m/z* 654.4 (M<sup>+</sup>).

#### [1-{PPh-(1'-*closo*-1', 2'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-*closo*-1, 2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (4)

To a solution of [*closo*-1, 2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] (300 mg, 2.08 mmol) in Et<sub>2</sub>O (15 mL) at 0 °C was added dropwise <sup>n</sup>BuLi (1.30 mL of a 1.6 M solution in hexanes, 2.08 mmol). The solution was stirred at 0 °C for 0.5 h before being warmed to room temperature and stirred for 1 h. The solution was then re-cooled to 0 °C before the dropwise addition of PPhCl<sub>2</sub> (0.14 mL, 1.04 mmol). The white suspension was stirred overnight and then heated to reflux for 2 h. Following filtration solvent was removed from the filtrate to afford a white

solid. The product was purified *via* preparative TLC (20:80, DCM:petrol;  $R_f = 0.65$ ) and isolated as a viscous white oil (40 mg, 10%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.79-7.75 (m, 1H,  $\text{C}_6\text{H}_5$ ), 7.69-7.57 (m, 3H,  $\text{C}_6\text{H}_5$ ), 7.53-7.49 (m, 1H,  $\text{C}_6\text{H}_5$ ), 3.65 (br s, 2H,  $\text{C}_{\text{cage}}\text{H}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.2 (2B), -1.9 (2B), -6.8 (4B), -10.1 (4B), -12.5 (8B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  55.5 (s). EIMS: envelope centered on  $m/z$  394.3 ( $\text{M}^+$ ).

**[BTMA][7-PPh<sub>2</sub>-nido-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([BTMA]X)**

Following the procedure established for the  $[\text{NMe}_4]^+$  salt of the same anion,<sup>11</sup> a solution of [1-PPh<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (500 mg, 1.52 mmol) in piperidine (7.52 mL, 76 mmol) was heated to reflux for 0.5 h before being allowed to cool and stir at RT for 0.5 h. Toluene (20 mL) then added and the reaction mixture was again heated to reflux, for 28 h. The solution was then concentrated to an oil *in vacuo* to remove excess piperidine. Toluene (5 mL) was added and the solution re-concentrated. This procedure was repeated a further two times to ensure the removal of piperidine which solubilises the product. The solid was then dissolved in ethanol (5 mL) and an aqueous solution of excess [BTMA]Cl added, affording a white precipitate which was filtered off. The filtrate was concentrated to an oil and water (5 mL) added to obtain a second crop of product. The white solids were combined and dried *in vacuo* (427 mg, 60%). Crystals suitable for diffraction were grown from a concentrated DCM solution layered with petrol at -20 °C. C<sub>24</sub>H<sub>37</sub>B<sub>9</sub>NP requires; C 61.6, H 7.97, N 2.99. Found for [BTMA]X; C 60.7, H 8.04, N 3.13%.  $^1\text{H}$  NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  7.86-7.27 (m, 15H,  $\text{C}_6\text{H}_5$ ), 4.49 (s, 2H,  $\text{CH}_2$ ), 3.10 (s, 9H,  $\text{CH}_3$ ), 1.88 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  -8.7 (1B), -9.4 (1B), -14.8 (2B), -15.6 (1B), -17.6 (1B), -20.4 (1B), -32.2 (1B), -36.0 (1B).  $^{31}\text{P}\{^1\text{H}\}$  NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  17.6 (s).

**[1-P(Se)Ph<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (IISe), [1,7-{P(Se)Ph<sub>2</sub>}<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (VISe<sub>2</sub>), [1-{1'-7'-P(Se)Ph<sub>2</sub>-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}-7-P(Se)Ph<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (2Se<sub>2</sub>) and [1-{P(Se)Ph-(1'-*closo*-1',2'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (4Se)**

These carboranylphosphine selenides were prepared by the general method of heating to reflux a solution of the appropriate carboranylphosphine in toluene with an excess (typically 10- to 30-fold) of elemental selenium for between 16 and 48 h. The excess Se was filtered off and washed with DCM. The filtrate and washings were combined and evaporated to dryness to afford the products as analytically-pure white solids.

[1-P(Se)Ph<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (IISe): From 0.31 mmol of phosphine was produced 82 mg of product. Yield 66%. C<sub>14</sub>H<sub>21</sub>B<sub>10</sub>PSe requires; C 41.3, H 5.20. Found for IISe; C 41.0, H 5.23%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27-8.22 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.59-7.48 (m, 6H,  $\text{C}_6\text{H}_5$ ), 2.97 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -4.1 (1B), -4.7 (1B), -9.8 (2B), -10.5 (2B), -12.3 (2B), -14.5 (2B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  45.2 (s + Se satellites,  $^1J_{\text{PSe}} = 797$  Hz). EIMS: envelope centered on  $m/z$  407.1 ( $\text{M}^+$ ). Single crystals grown from slow evaporation of a fluorobenzene solution.

[1,7-{P(Se)Ph<sub>2</sub>}<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (VISe<sub>2</sub>): From 0.22 mmol of phosphine was produced 110 mg of product. Yield 57%. C<sub>26</sub>H<sub>30</sub>B<sub>10</sub>P<sub>2</sub>Se<sub>2</sub> requires; C 46.6, H 4.51. Found for VISe<sub>2</sub>; C 46.6, H 4.63%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.21-8.15 (m, 8H,  $\text{C}_6\text{H}_5$ ), 7.58-7.46 (m, 12H,  $\text{C}_6\text{H}_5$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -2.6 (2B), -9.2 (6B), -12.3 (2B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  46.4 (s + Se satellites,  $^1J_{\text{PSe}} = 804$  Hz). EIMS: envelope centered on  $m/z$  670.1 ( $\text{M}^+$ ). Single crystals grown from a concentrated DCM solution.

[1-{1'-7'-P(Se)Ph<sub>2</sub>-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}-7-P(Se)Ph<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (2Se<sub>2</sub>): From 0.03 mmol of phosphine was produced 17 mg of product. Yield 68%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.16-8.11 (m, 8H,  $\text{C}_6\text{H}_5$ ), 7.52-7.45 (m, 12H,  $\text{C}_6\text{H}_5$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.8 to -3.7 (2B), -3.7 to -6.9 (2B), -6.9 to -18.8 (16B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  46.2 (s + Se satellites,  $^1J_{\text{PSe}} = 802$  Hz). EIMS: envelope centered on  $m/z$  813.4 ( $\text{M}^+$ ). Crystals grown from a concentrated DCM solution layered with petrol at -20 °C.

[1-{P(Se)Ph-(1'-*closo*-1',2'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (4Se): From 0.10 mmol of phosphine was produced 20 mg of product. Yield 42%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.30-8.24 (m, 1H,  $\text{C}_6\text{H}_5$ ), 8.09-8.04 (m, 1H,  $\text{C}_6\text{H}_5$ ), 7.78-7.49 (m, 3H,  $\text{C}_6\text{H}_5$ ), 4.67 (br s, 2H,  $\text{C}_{\text{cage}}\text{H}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.3 (2B), -2.4 (2B), -6.8

(4B), -10.2 (4B), -12.7 (8B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  68.2 (s + Se satellites,  $^1J_{\text{PSe}} = 846$  Hz). EIMS: envelope centered on  $m/z$  473.3 ( $\text{M}^+$ ). Crystals from slow evaporation of a petrol solution.

[1-(1'-*closo*-1',7'- $\text{C}_2\text{B}_{10}\text{H}_{11}$ )-7-P(Se)Ph $_2$ -*closo*-1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ] (**1Se**)

Elemental selenium (161 mg, 1.91 mmol) was added to a  $\text{CDCl}_3$  solution (0.8 mL) of **1** (30 mg, 0.064 mmol) in a J. Young NMR tube. The mixture was heated to 70 °C overnight, following which the solution was filtered to remove excess selenium, subsequently washed with DCM. The combined solutions were then concentrated to a white solid (31 mg, 90%). Crystals suitable for a diffraction study were grown from a concentrated solution of DCM layered with petrol at -20 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.24-8.19 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.60-7.50 (m, 6H,  $\text{C}_6\text{H}_5$ ), 2.94 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.1 to -6.5 (3B), -6.5 to -20.8 (17B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  46.2 (s + Se satellites,  $^1J_{\text{PSe}} = 802$  Hz).  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -204.65 (d,  $^1J_{\text{PSe}} = 803$  Hz). EIMS: envelope centered on  $m/z$  549.3 ( $\text{M}^+$ ).

[1-P(Se)(H)'Bu-*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ] (**3Se**)

Carboranylphosphine [1-P'Bu $_2$ -*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ] (**VIII**, 260 mg, 0.9 mmol) was dissolved in toluene (15 mL) and elemental selenium (710 mg, 9.0 mmol) was added. The suspension was heated to reflux overnight before being allowed to cool to room temperature. The excess selenium was filtered off and washed with DCM. The combined solutions were evaporated to yield a yellow solid (130 mg, 46%). Crystals suitable for diffraction were grown from slow evaporation of a concentrated solution in DCM.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.33 (d,  $^1J_{\text{PH}} = 468$  Hz, 1H, PH), 4.75 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ), 1.43 [d,  $^3J_{\text{PH}} = 36$  Hz, 9H,  $\text{C}(\text{CH}_3)_3$ ].  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.2 (1B), -2.4 (1B), -6.5 (1B), -7.4 (1B), -10.6 (1B), -11.8 (3B), -13.6 (1B), -14.4 (1B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  58.0 (s + Se satellites,  $^1J_{\text{PSe}} = 792$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  58.0 (d,  $^1J_{\text{PH}} = 468$  Hz). EIMS: envelope centered on  $m/z$  312.1 ( $\text{M}^+$ ).

[1-P(Se)('Bu) $_2$ -*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ] (**VIIISe**)

Compound **VIII** (12 mg, 0.05 mmol) was dissolved in  $\text{C}_6\text{D}_6$  (0.7 mL) in a J. Young NMR tube, and selenium (41 mg, 0.52 mmol) was added. The tube was thoroughly shaken and left at room temperature for 16 days, at which time the reaction was judged to have gone to completion by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Excess Se was removed by filtration prior to NMR analysis.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.54 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ), 1.20 [d,  $^3J_{\text{PH}} = 16.0$  Hz, 18H,  $\text{C}(\text{CH}_3)_3$ ].  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.9 (1B), -1.7 (1B), -7.8 (2B), -9.4 (2B), -11.0 (2B), -12.9 (2B).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  106.0 (s + Se satellites,  $^1J_{\text{PSe}} = 777$  Hz).  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -287.5 (d,  $^1J_{\text{PSe}} = 777$  Hz).

[BTMA][7-P(Se)Ph $_2$ -*nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{11}$ ] ([BTMA]**XSe**)

The carboranylphosphine selenide **1Se** (120 mg, 0.29 mmol) was dissolved in ethanol (30 mL) and piperidine (0.28 mL, 2.9 mmol) added. The solution was heated to reflux overnight then cooled to room temperature and evaporated to a colourless oil. Excess piperidine was removed by dissolving the oil in the minimal volume of toluene and evaporating the solution *in vacuo*. The oil was then dissolved in ethanol (10 mL) and an excess aqueous solution of [BTMA]Cl was added. A white precipitate formed which was collected by filtration and isolated (70 mg, 44%). Single crystals were grown from a concentrated DCM solution layered with petrol at -20 °C.  $\text{C}_{24}\text{H}_{37}\text{B}_9\text{NPSe}$  requires; C 52.7, H 6.82, N 2.56. Found for [BTMA]**XSe**; C 52.2, H 6.91, N 2.57%.  $^1\text{H}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  7.94-7.11 (m, 15H,  $\text{C}_6\text{H}_5$ ), 4.75 (s, 2H,  $\text{CH}_2$ ), 3.32 (s, 9H,  $\text{CH}_3$ ), 2.43 (br s, 1H,  $\text{C}_{\text{cage}}\text{H}$ ), -2.63 (br s, 1H, BHB).  $^{11}\text{B}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  -8.5 (1B), -10.0 (1B), -13.3 (1B), -14.4 (2B), -18.4 (1B), -19.2 (1B), -31.2 (1B), -35.5 (1B).  $^{31}\text{P}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  50.1 (s + Se satellites,  $^1J_{\text{PSe}} = 737$  Hz).

### Crystallographic Studies

Methods used to obtain single crystals suitable for diffraction have been noted above for each new species. In addition we have crystallographically characterized the known carboranylphosphine [1-PPh $_2$ -*closo*-1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ] (**II**) using crystals grown from the slow evaporation of a DCM-petrol solution. All crystals were



obtained without occluded solvent except for **4Se**, which crystallized with 0.5 molecules of 2,3-dimethylbutane per asymmetric unit, i.e. **4Se**·0.5C<sub>6</sub>H<sub>14</sub>. Diffraction data from compounds **2**, **3Se**, **ISe** and **VISe<sub>2</sub>** and salts [BTMA]**X** and [BTMA]**XSe** were collected at 100 K using a Bruker X8 APEXII diffractometer operating with Mo-*K<sub>α</sub>* X-radiation. Data from **1Se**, **2Se<sub>2</sub>** and **4Se**·0.5C<sub>6</sub>H<sub>14</sub> were measured at 120 K on a Rigaku Oxford Diffraction SuperNova diffractometer at the University of Edinburgh, the first two using Mo-*K<sub>α</sub>* and the last Cu-*K<sub>α</sub>* radiation. Data from **II** were obtained at 150 K on a Bruker D8 Venture diffractometer equipped with Mo-*K<sub>α</sub>* radiation at the University of Glasgow. All samples were single crystals except for **2**, [BTMA]**XSe** and **ISe**, each of which crystallized as two-component twins. Using *OLEX2*<sup>14</sup> structures were solved by direct methods using the *SHELXS*<sup>15</sup> or *SHELXT*<sup>16</sup> program, and refined by full-matrix least-squares using *SHELXL*.<sup>17</sup> In all cases the crystallographic models were fully ordered. Cage C atoms bearing only H substituents were clearly distinguished from B atoms using both the *Vertex-Centroid Distance* (VCD) and *Boron-Hydrogen Distance* (BHD) methods,<sup>18</sup> requiring positional refinement of C<sub>cage</sub>H and BH atoms. In **3Se** the PH atom and in [BTMA]**X** and [BTMA]**XSe** the BHB bridging atoms were also positionally refined. All other H atoms were treated as riding on their respective C atom, with C<sub>primary</sub>-H 0.98 Å, C<sub>secondary</sub>-H 0.99 Å, C<sub>tertiary</sub>-H 1.00 Å and C<sub>phenyl</sub>-H 0.95 Å. H atom displacement parameters were constrained to 1.2×*U*<sub>eq</sub> (bound B or C) except for Me H atoms, 1.5×*U*<sub>eq</sub> (C<sub>methyl</sub>). Views of molecules whose structures are reported here were drawn with *OLEX2*. [Figure 4](#) was drawn with Mercury,<sup>19</sup> using coordinates retrieved from the CSD.<sup>20</sup> The Supporting Information contains unit cell data and further experimental details.

### Computational Studies

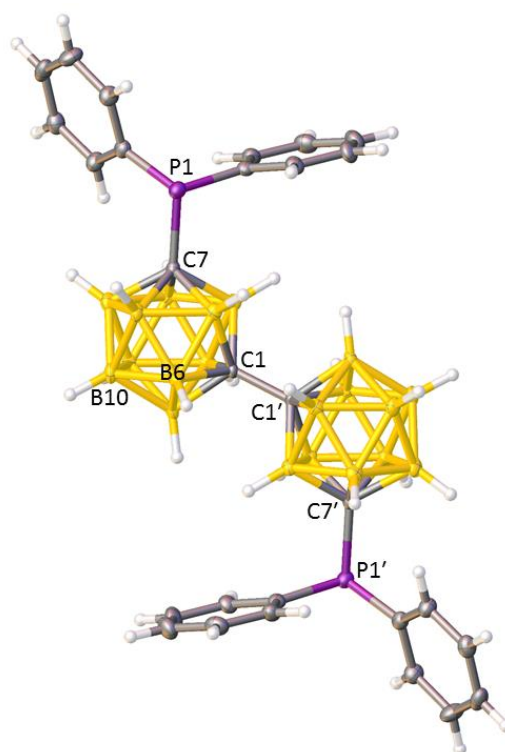
All calculations used the Jaguar package<sup>21</sup> and the standard Becke-Perdew (BP86)<sup>22</sup> density functional. The 6-31G\* basis set was used for all atoms, along with the polarisable continuum model (PCM) as implemented in Jaguar,<sup>22e</sup> using ethanol as the solvent. “Loose” convergence (5 times larger than default criteria) was used for all geometry optimizations. See SI for full computational details and additional discussion.



## ■ RESULTS AND DISCUSSION

### Preparation and Characterization of Carboranylphosphines

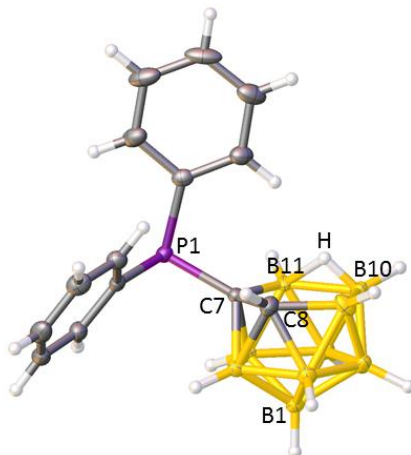
The deprotonation of [1-(1'-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>], trivial name 1,1'-bis(*meta*-carborane),<sup>12</sup> in toluene with slightly more than one equivalent of <sup>n</sup>BuLi followed by reaction with ClPPh<sub>2</sub> affords, after work-up involving thin-layer chromatography (TLC), as major product (28%), the monosubstituted species [1-(1'-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (**1**) and, as minor product (7%), the disubstituted [1-(1'-7'-PPh<sub>2</sub>-*closo*-1',7'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)-7-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (**2**). If the same reaction is performed using three equivalents of <sup>n</sup>BuLi and of ClPPh<sub>2</sub> the same two species are obtained but in equal yields (11% after TLC). Both products are readily isolated in pure form by TLC. Compound **1** was characterized by mass spectrometry and <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. Notable in the <sup>1</sup>H NMR spectrum is a broad singlet at δ 2.91 of relative integral one assigned to C<sub>cage</sub>H. Compound **2** was similarly characterized (no C<sub>cage</sub>H resonance was observed) and, in addition, a single-crystal X-ray diffraction study was undertaken. A perspective view of a single molecule of **2** is shown in Figure 1. The molecule has crystallographically-imposed C<sub>i</sub> symmetry about the mid-point of the C1–C1' bond, requiring that the C7···C1–C1'···C7' and P1···C1–C1'···P1' torsion angles are 180°. A similar orientation was observed by Stadlbauer *et al.* for bis(amino)phosphine and aminophosphinite derivatives of 1,1'-bis(*meta*-carborane),<sup>12c</sup> which also share very similar C1–C1' and C7–P1 distances to those in **2**.



**Figure 1.** Perspective view of compound **2** with displacement ellipsoids drawn at the 50% probability level except for H atoms. The molecule has crystallographically-imposed  $\bar{1}$  ( $C_i$ ) symmetry about the mid-point of the C1–C1' bond. Important interatomic distances (Å): C1–C1' 1.528(6), C7–P1 1.886(3).

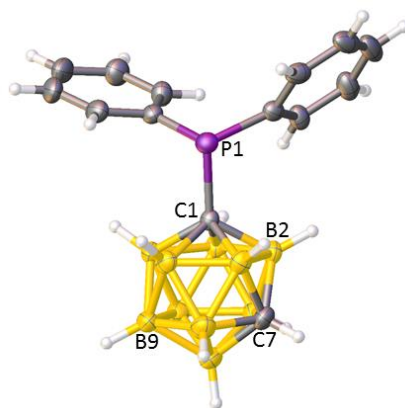
We have previously described compound **XI**, a species in which a {PPh} fragment bridges between C2 and C2' of 1,1'-bis(*ortho*-carborane) forming a 5-membered ring.<sup>8</sup> Our next target was an analogous compound but one in which the two *ortho*-carborane cages were not linked. Deprotonation of [*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] with one equivalent of <sup>n</sup>BuLi followed by treatment with 0.5 equivalents of PPhCl<sub>2</sub> afforded [1-{PPh-(1'-*closo*-1',2'-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (**4**) as a viscous oil following work-up, characterized by mass spectrometry and <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P NMR spectroscopies. Note that the analogous species with Me groups attached to C2 and C2', **XII**, has been reported by Teixidor, Viñas and co-workers<sup>11</sup> and subsequently crystallographically characterized by the same group.<sup>23</sup>

It would be reasonable to expect that the basicity of a carboranylphosphine would change markedly on deboronation of the carborane to form a nido anion. We therefore prepared [BTMA][7-PPh<sub>2</sub>-*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([BTMA]**X**) (BTMA = benzyltrimethylammonium) by mild deboronation of [1-PPh<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] with piperidine followed by metathesis with [BTMA]Cl, based on the procedure established for the analogous [NMe<sub>4</sub>]<sup>+</sup> salt.<sup>11</sup> The product was obtained in 60% yield as a white crystalline solid which was characterized by elemental analysis, <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P NMR spectroscopies, and ultimately by single-crystal X-ray diffraction (Figure 2). In the carboranylphosphine anion **X**<sup>-</sup> the B10–B11 connectivity is bridged asymmetrically by H.



**Figure 2.** Perspective view of the anion of [BTMA]**X** ([BTMA] cation omitted for clarity). Displacement ellipsoids as in Figure 1. Important interatomic distances (Å): C7–C8 1.586(3), C7–P1 1.8388(19), B10–B11 1.768(3), B10–H 1.04(2), B11–H 1.32(2).

Finally, we have resynthesized and structurally characterized the known carboranylphosphine [1-PPh<sub>2</sub>-*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (**II**). The original synthesis used only 0.3 equivalents of ClPPh<sub>2</sub> and reported a yield of 23%.<sup>13</sup> Using stoichiometric amounts of reagents we obtain an isolated yield of 57%. The molecular structure is shown in Figure 3. The C1–P1 distance, 1.8770(13) Å, stands in excellent comparison with reported C<sub>cage</sub>–PPh<sub>2</sub> distances in derivatives of both [*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>]<sup>24</sup> and [*closo*-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>].<sup>25</sup>



**Figure 3.** Perspective view of compound **II**. Displacement ellipsoids as in Figure 1. Important interatomic distance (Å): C1–P1 1.8770(13).

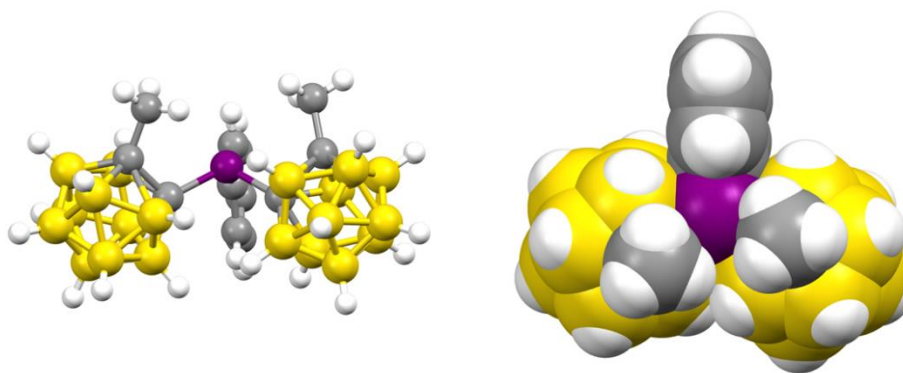
### Preparation and Characterization of Carboranylphosphine Selenides

Phosphine selenides are usually conveniently prepared by simply heating the phosphine with an excess of elemental Se, frequently in toluene.<sup>6</sup> This method was successfully employed to prepare the new species **IISe**, **VIISe<sub>2</sub>** and **2Se<sub>2</sub>** in isolated yields of 57–68%. All three compounds were characterized by mass spectrometry and <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies, and the identities of **IISe** and **VIISe<sub>2</sub>** were also confirmed by elemental analysis. Notable in the <sup>31</sup>P{<sup>1</sup>H} spectra are both a downfield shift in the resonance relative to that of the free phosphine ( $\Delta\delta$  typically ca. 25 ppm) and the appearance of satellites due to <sup>1</sup>J<sub>PSe</sub> coupling. We will use the magnitude of this coupling as a measure of phosphine basicity, as discussed in the following section. As far as we are aware **VIISe<sub>2</sub>** is the first example of double selenation of a carboranylbis(phosphine). Viñas and co-workers reacted **VI** with two equivalents of Se under relatively mild conditions and only one P was selenated.<sup>7</sup> We repeated their reaction under much more forcing conditions (20 eq. Se, toluene reflux, 20 h) but again only the monoselenated **VISe** was formed. Presumably the diselenide of **VI** is simply too sterically-congested.

Surprisingly, heating to reflux a toluene solution of the bis(carboranyl)phosphine **XII** with excess Se did not result in any reaction, as monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. In attempting to understand this non-reaction we have examined the structure of **XII** determined crystallographically.<sup>23</sup> As shown in **Figure 4 left** the molecule is oriented such that the Ph group lies in the approximate molecular mirror plane and the Me groups on the carborane units are syn with respect to each other and to the lone pair of electrons on P. **Figure 4 right** shows a space-filling representation of the molecule looking down on the lone pair. We believe that there is simply insufficient space for a Se atom to approach P to form the selenide. Support for this assumption comes from % *V*<sub>bur</sub> calculations<sup>26</sup> on phosphines **XI** (% *V*<sub>bur</sub> = 32.0, does selenate<sup>8</sup>), PMes<sub>3</sub> (% *V*<sub>bur</sub> = 49.2, does not selenate<sup>27</sup>) and **XII** (% *V*<sub>bur</sub> = 52.2, does not selenate). While it is always dangerous to attempt to rationalize reactions (or non-reactions) in solution on the basis of a solid-state molecular structure, it is likely that the molecular orientation observed in the crystal structure of **XII** is maintained in solution. Although the Ph resonances in the <sup>1</sup>H NMR spectrum of **XII** are reported as simply (m, 5H, C<sub>6</sub>H<sub>5</sub>)<sup>11</sup> we believe that the crowded nature of the molecule means that the Ph group is not freely rotating. This is because in the less-crowded, non-Me analog of **XII**, compound **4**, the Ph resonances fall into three well-defined groups (m 1H, m 3H and m 1H), which can only be interpreted in terms of no rotation about the P–Ph bond. This is supported by analysis of the calculated geometry for **XII**, which highlights close steric

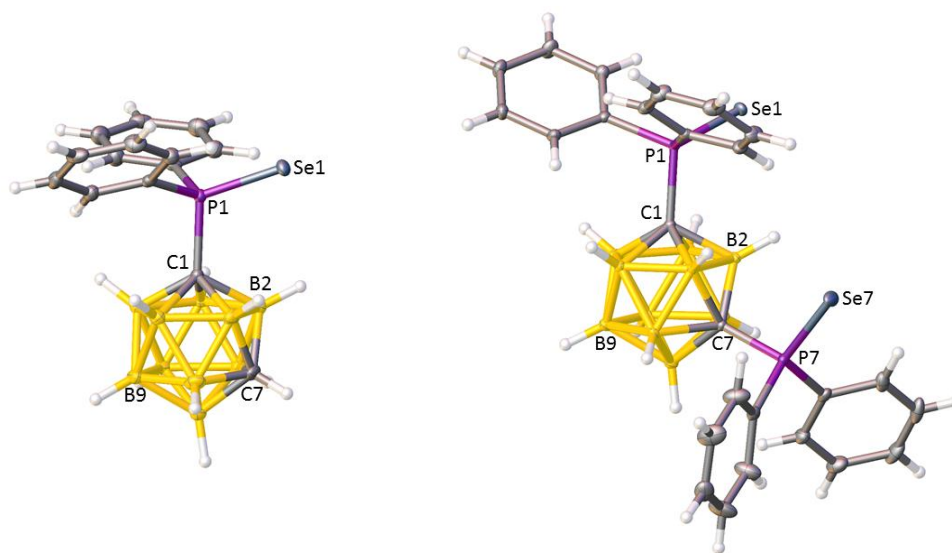
interactions when the Ph ring is rotated to lie perpendicular to the phosphorus lone pair (see ESI for details and images). Even though compound **4** displays a degree of stereochemical rigidity, the fact that the C2 and C2' cage atoms are not methylated means that formation of the selenide is not sterically-blocked, and compound **4Se** is obtained in 42% yield by the standard method of heating to reflux a solution of **4** in toluene with excess Se.

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**Figure 4.** (left) Perspective view of compound **XII** showing the relative orientation of Ph and carboranyl groups about the phosphorus centre. (right) Space-filling representation of **XII** viewed looking down on the phosphorus lone pair.

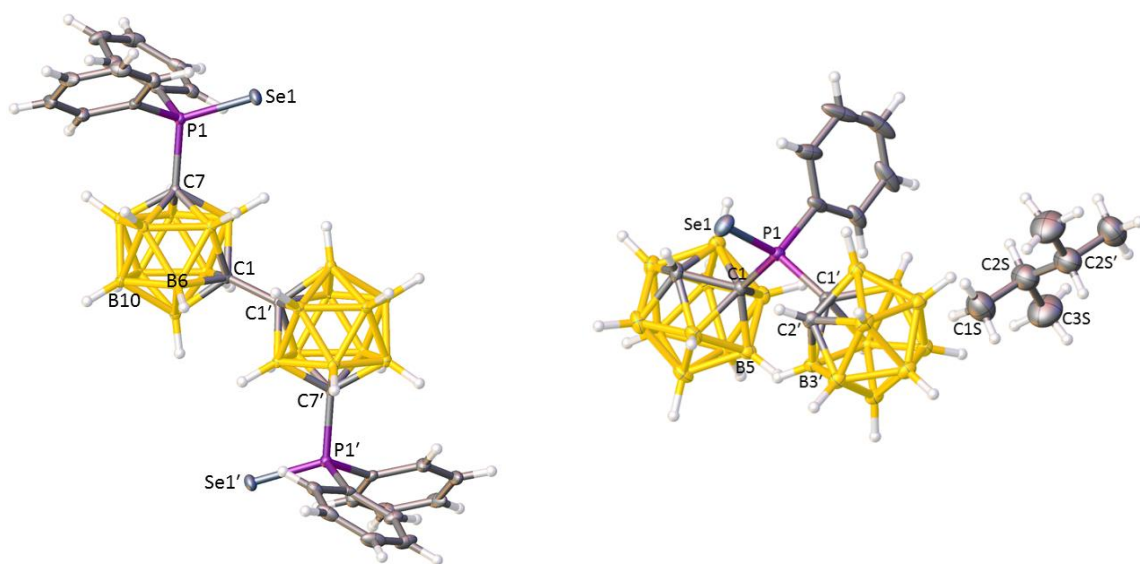
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**Figure 5.** (left) Perspective view of one of two crystallographically-independent molecules of compound **IISe**. Displacement ellipsoids as in Figure 1. Important interatomic distances (Å): C1–P1 1.878(2), P1–Se1 2.1054(6), C1'–P1' 1.873(2), P1'–Se1' 2.1018(6). (right) Perspective view of compound **VISe<sub>2</sub>**. Displacement ellipsoids as in Figure 1. Important interatomic distances (Å): C1–P1 1.8816(13), P1–Se1 2.0988(3), C7–P7 1.8813(13), P7–Se7 2.0957(4).

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The selenides **IISe**, **VIISe<sub>2</sub>**, **2Se<sub>2</sub>** and **4Se** were also studied crystallographically, and perspective views of single molecules together with key molecular parameters are provided in Figures 5 and 6. All structures were fully-ordered and in **IISe** and **4Se** the cage CH vertices were unambiguously identified by standard methods.<sup>18</sup> An unexpected finding in the crystallographic study of **4Se** was the presence of 2,3-dimethylbutane (DMB) in the lattice located on a crystallographic inversion centre. Thus one half-molecule of DMB co-crystallizes with one molecule of **4Se**. DMB (b.p. 57.9 °C) is a component of the petrol (40-60 petroleum ether) from which crystals were grown by slow evaporation, and presumably the lattice formed by the **4Se** molecules contains a cavity of the appropriate size and shape to accommodate the DMB solvate. There are only three entries for 2,3-dimethylbutane on the Cambridge Structural Database (CSD).<sup>20</sup> An early study of DMB at 80 K reports unit cell dimensions but no space group and no atomic coordinates.<sup>28</sup> More recently DMB has been forced into a Sc-based metal-organic framework at high pressure and studied crystallographically at 0.2 GPa and 0.4 GPa.<sup>29</sup> However, both determinations of the DMB are imprecise and there is disorder, a consequence of which is that the molecule appears to be planar at the tertiary C atoms. In **4Se**·0.5DMB the DMB molecule is fully ordered, and the present determination therefore represents the only current crystallographic study of 2,3-dimethylbutane which is both accurate and precise.

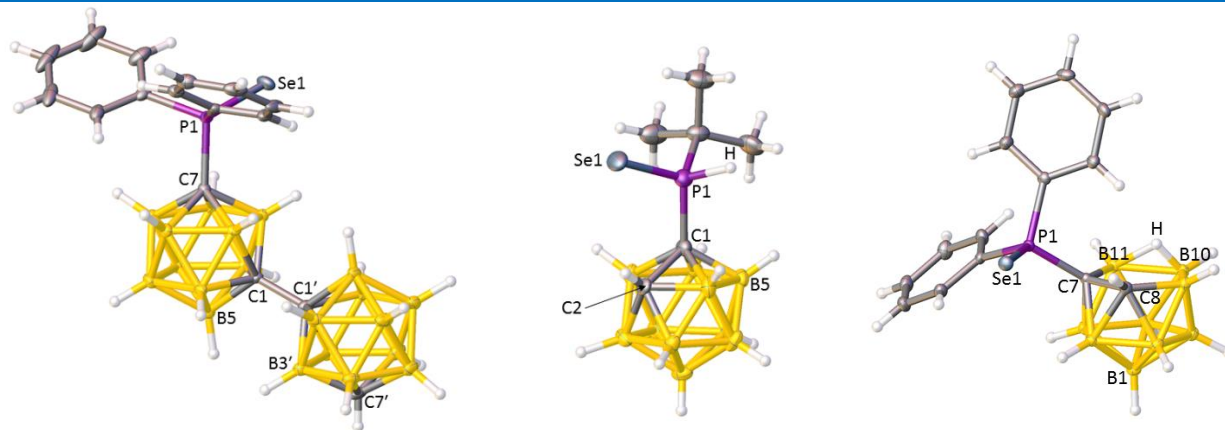


**Figure 6.** (left) Perspective view of compound **2Se<sub>2</sub>**. Displacement ellipsoids as in Figure 1. The molecule has crystallographically-imposed  $\bar{1}$  ( $C_i$ ) symmetry about the mid-point of the C1–C1' bond. Important interatomic distances (Å): C1–C1' 1.524(4), C7–P1 1.890(2), P1–Se1 2.1009(6). (right) Perspective view of compound **4Se** together with the whole of the 2,3-dimethylbutane solvate [crystallographically-imposed  $\bar{1}$  ( $C_i$ ) symmetry about the mid-point of the C2S–C2S' bond]. Displacement ellipsoids as in Figure 1. Important interatomic distances (Å): C1–C2 1.666(3), C1–P1 1.900(2), C1'–C2' 1.659(3), C1'–P1 1.890(2), P1–Se1 2.0845(5), C1S–C2S 1.511(5), C2S–C3S 1.532(5), C2S–C2S' 1.514(7).

Compound **1Se**, the selenide of the monophosphine derivative of 1,1'-bis(*meta*-carborane), was afforded in high yield by heating a CDCl<sub>3</sub> solution of **1** with Se in a J. Young NMR tube at 70 °C. After isolating the product from excess Se, spectroscopic characterization confirmed the nature of **1Se** by the observation of a downfield shift of ca. 25 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and the presence of associated Se satellites.



Independently, the magnitude of the P-Se coupling was determined by a  $^{77}\text{Se}$  NMR study revealing a simple doublet resonance. The structure of **1Se** established crystallographically is shown in Figure 7, left.



**Figure 7.** Perspective view of the selenides (left) **1Se**, (center) **3Se** and (right) **XSe<sup>-</sup>**. Displacement ellipsoids as in Figure 1. Important interatomic distances (Å): **1Se** C1–C1' 1.533(4), C7–P1 1.889(3), P1–Se1 2.0907(8). **3Se** C1–C2 1.654(7), C1–P1 1.870(5), P1–Se1 2.0953(15), P1–H 1.43(2). **XSe<sup>-</sup>** C7–C8 1.566(3), C7–P1 1.824(2), P1–Se1 2.1171(6), B10–B11 1.842(3), B10–H 1.08(3), B11–H 1.46(3).

Wishing to prepare the selenide of a carboranylphosphine with two large, electron-donating groups also attached to the P atom we heated to reflux a toluene solution of the compound [1-P<sup>*t*</sup>Bu<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (**VIII**)<sup>10</sup> with an excess of elemental selenium. After the usual work-up the product was isolated as a yellow solid. Spectroscopic analysis, however, quickly revealed that the expected species **VIIISe** had not been formed. While the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed a singlet with  $^{77}\text{Se}$  satellites the resonance was shifted *upfield* from that in **VIII**, from  $\delta$  94.8<sup>10</sup> to 58.0. In the  $^1\text{H}$  NMR spectrum, in addition to the broad singlet at  $\delta$  4.75 for C<sub>cage</sub>H was a large doublet at  $\delta$  6.33 ( $J$  = 468 Hz) also integrating to 1H, with the 9 <sup>*t*</sup>Bu protons appearing as a smaller doublet ( $J$  = 36 Hz). These data were consistent with the presence of a {P(Se)(H)<sup>*t*</sup>Bu} fragment, with the large doublet due to  $^1J_{\text{PH}}$  and the smaller doublet due to  $^3J_{\text{PH}}$ . Confirmation was afforded by a  $^{31}\text{P}$  NMR spectrum, in which the sharp central singlet in the  $^{31}\text{P}\{^1\text{H}\}$  spectrum gave way to a broad doublet,  $J$  = 468 Hz, with the  $^3J_{\text{PH}}$  coupling not resolved. Thus the product was identified as [1-P(Se)(H)<sup>*t*</sup>Bu-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (**3Se**), with confirmation subsequently afforded by mass spectrometry and a single-crystal X-ray diffraction study (Figure 7, center). In principle, loss of a <sup>*t*</sup>Bu group and its replacement by H (possibly via  $\beta$ -elimination) could occur from **VIII** directly or from its selenide, once formed, under the conditions of the reaction. However **VIII** was found to be stable in refluxing toluene for ca. 72 h while [1-P(Se)<sup>*t*</sup>Bu<sub>2</sub>-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (**VIIISe**), subsequently successfully prepared by performing the reaction at room temperature, degrades to **3Se** when heated to reflux in toluene overnight. Note that [1-P(Se)(H)R-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>] (R = <sup>*i*</sup>Pr, Cy), compounds analogous to **3Se**, are formed by decomposition of the dimeric species [ $\mu_{1,2}$ -SeP(R)Se-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]<sub>2</sub> in refluxing toluene.<sup>30</sup> Note also that **VIIISe** was prepared in a small-scale reaction (12 mg of **VIII** in C<sub>6</sub>D<sub>6</sub> in a J. Young NMR tube) so no yield was determined, but the product was thoroughly characterized by multinuclear NMR spectroscopy.

Our final synthetic target was an anionic nido carboranylphosphine selenide, currently unknown in the literature. Trials involving direct reaction of the nido anion **X<sup>-</sup>** (as its [NMe<sub>4</sub>]<sup>+</sup> salt) with Se did not provide any evidence of P–Se bond formation from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. This leaves deboronation after selenation as the only viable route. The established fragility of the P–C<sub>cage</sub> bond in carboranylphosphines<sup>11</sup>

requires a mild deboronation protocol similar to that used to prepare  $\mathbf{X}^-$ , but to avoid excessive amounts of piperidine we heated **ISe** in an ethanol/piperidine solution.<sup>11</sup> On work-up the product, [7-P(Se)Ph<sub>2</sub>-*nido*-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> as its [BTMA]<sup>+</sup> salt ([BTMA]**XSe**), was isolated as a white powder in 44% yield.

[BTMA]**XSe** was characterized by elemental analysis, NMR spectroscopies and single-crystal X-ray diffraction. In the <sup>1</sup>H NMR spectrum are broad integral-1 singlets for C<sub>cage</sub>H and BHB atoms at  $\delta$  2.43 and -2.63 respectively. The central singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is shifted downfield by ca. 32 ppm relative to that in [BTMA]**X** and is accompanied by the usual <sup>77</sup>Se satellites. Figure 7, right shows a perspective view of the anion.

### The Basicity of Carboranylphosphines

The primary objective of this study was to vary systematically carboranylphosphines and to investigate the effect this has on phosphine basicity, for reasons described in the Introduction. Historically there have been many methods used to establish a rank order of phosphine basicity including: the estimation of pK<sub>a</sub> values (of the conjugate acid) by potentiometric measurements;<sup>31</sup> measurement of CO stretching frequencies in phosphine complexes such as [Ni(L)(CO)<sub>3</sub>];<sup>32</sup> measurement of coupling constants between <sup>31</sup>P and other NMR-active nuclei such as <sup>11</sup>B<sup>33</sup> or <sup>195</sup>Pt<sup>6a</sup>; and experimental and computational determinations of proton affinities, PA.<sup>34</sup> However, one of the most convenient and popular experimental methods is to convert the phosphine to its selenide and indirectly assess the phosphine basicity via measurement of the <sup>1</sup>J<sub>PSe</sub> coupling constant,<sup>6</sup> the approach we have used here. Our study would include both new and literature carboranylphosphine selenides. In a small number of cases, the carboranylphosphine selenide is unknown, so we have also calculated the solvated proton affinity of a large number of carboranylphosphines with DFT (see computational details and EI for further information and discussion), to establish a correlation between PA and <sup>1</sup>J<sub>PSe</sub> for these species which can be used as a surrogate for <sup>1</sup>J<sub>PSe</sub> for those species where the selenide is unknown (**III**, **XII**), the simple monoselenide is unknown (**VII**, **2**), or, indeed, the carboranylphosphine is unknown (**XIII**, **XIV**, **XV**, **XVI**, **XVII**).

**Table 1.** Carboranylphosphines, Selenides, <sup>1</sup>J<sub>PSe</sub> Coupling Constants and Calculated Proton Affinities

Carboranylphosphine	Selenide	<sup>1</sup> J <sub>PSe</sub> /Hz (selenide)	PA/kcal mol <sup>-1</sup> (phosphine)	Ref (selenide)
<b>I</b>	<b>ISe</b>	799	265.3	3
<b>II</b>	<b>IISe</b>	797	269.0	this work
<b>III</b>	– <sup>a</sup>	–	270.3	this work
<b>IV</b>	<b>IVSe</b>	804	265.0	7
<b>V</b>	<b>VSe</b>	812	266.6	7
<b>VI</b>	<b>VISe</b>	807	265.5	7
<b>VII</b>	– <sup>b</sup>	–	268.9	this work
<b>VII</b>	<b>VIISe<sub>2</sub></b>	804	–	this work
<b>1</b>	<b>1Se</b>	802	268.4	this work
<b>2</b>	– <sup>b</sup>	–	267.2	this work
<b>2</b>	<b>2Se<sub>2</sub></b>	802		this work
<b>3</b>	<b>3Se</b>	792	262.6	this work
<b>VIII</b>	<b>VIIISe</b>	777	274.0	this work
<b>IX</b>	<b>IXSe</b>	704	280.3	3
<b>X<sup>-</sup></b>	<b>XSe<sup>-</sup></b>	737	279.9	this work
<b>XI</b>	<b>XISe</b>	891	248.8	8
<b>XII</b>	– <sup>a</sup>	–	249.4	this work
<b>4</b>	<b>4Se</b>	846	248.9	this work
<b>XIII<sup>c</sup></b>	–	–	270.7	this work
<b>XIV<sup>c</sup></b>	–	–	269.9	this work

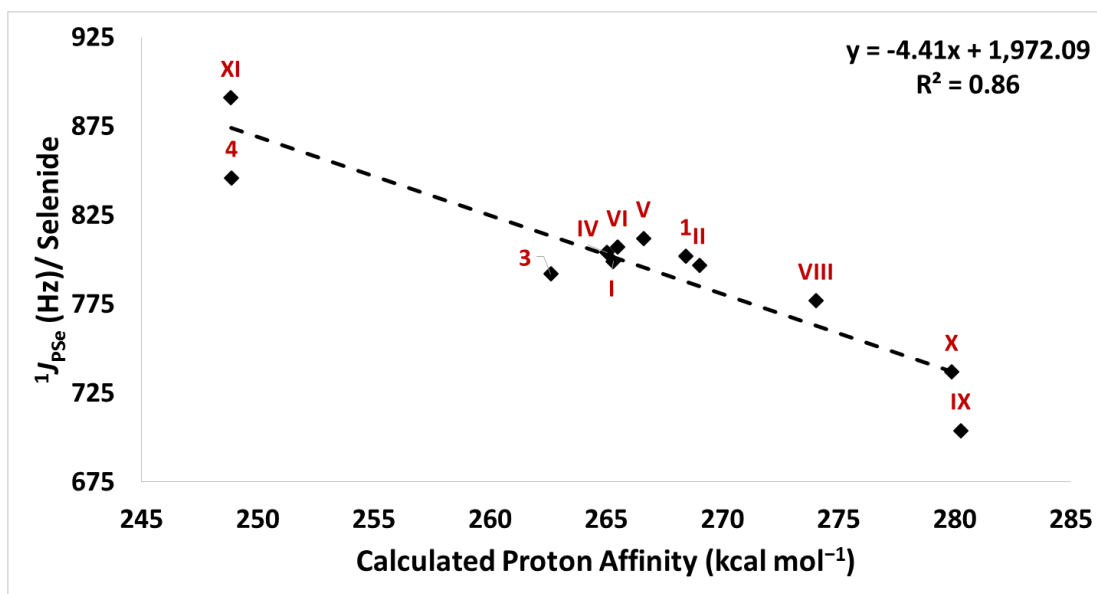


<b>XV</b> <sup>c</sup>	—	—	269.6	this work
<b>XVI</b> <sup>c</sup>	—	—	285.4	this work
<b>XVII</b> <sup>c</sup>	—	—	234.4	this work

<sup>a</sup> selenide not known. <sup>b</sup> monoselenide not known. <sup>c</sup> carboranylphosphine not known.

**Table 1** summarises the carboranylphosphines considered, together with their calculated PA values and the magnitudes of the  $^1J_{\text{PSe}}$  coupling constants of their selenides. Note that the sign of  $^1J_{\text{PSe}}$  has been determined to be negative<sup>35</sup> but is conventionally reported as the modulus, a convention we will follow.

The direct correlation between  $^1J_{\text{PSe}}$  in a phosphine selenide and  $\text{p}K_{\text{b}}$  of the corresponding phosphine is well-established and Figure 1 of reference 6b provides a convenient representation of that correlation (note that the datum point for  $\text{P}^t\text{Bu}_3$  appears to have been misplotted). Thus the stronger the base the smaller the magnitude of  $^1J_{\text{PSe}}$ . In **Figure 8** we show  $^1J_{\text{PSe}}$  vs. calculated PA for those carboranylphosphine selenides in **Table 1** for which both data are known (excluding diselenides). Although there are a small number of slightly more pronounced outliers (**3**, **4**, **IX**, **XI**), the relationship between these parameters is described rather well by a straight line, confirming that there is a reasonable inverse correlation between  $^1J_{\text{PSe}}$  and PA with linear regression yielding  $R^2 = 0.86$ . This again confirms that the stronger the base the smaller the magnitude of  $^1J_{\text{PSe}}$ , and provides us with an alternative means of rank-ordering carboranylphosphine basicities if the selenide is unknown or synthetically inaccessible.



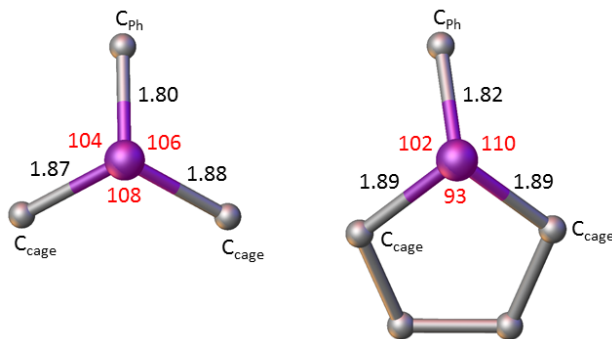
**Figure 8.** Plot of  $^1J_{\text{PSe}}$  (Hz) versus calculated PA ( $\text{kcal mol}^{-1}$ , see SI for further discussion) for the known carboranylphosphine selenides and their parent carboranylphosphines, respectively (data in Table 2).

#### Changing the groups attached to P

In carboranylphosphines **I** and **4** two of the groups bound to the P atom are common, Ph and 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ , while the third group R varies. Replacing R = Ph in **I** by R = 1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$  to give **4**, has a dramatic effect on  $^1J_{\text{PSe}}$  of the corresponding selenides with coupling constants of 799 and 846 Hz, respectively, measured. This is fully consistent with a C-bound carborane group being strongly electron-

withdrawing, making **4** only weakly basic. Note that Spokoyny and co-workers have previously found that, based on calculated charges of P atoms in phosphines, the *closo*-1,7- $\text{C}_2\text{B}_{10}\text{H}_{11}$  group is more electron-withdrawing than  $\text{C}_6\text{F}_5$ ,<sup>5e</sup> and we have previously shown that, as measured by  $^1J_{\text{PSe}}$  values, the *closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  group is also more electron-withdrawing than  $\text{C}_6\text{F}_5$ .<sup>3</sup> The calculated PAs of **I**, **4** and  $\text{PPh}_2(\text{C}_6\text{F}_5)$ ,<sup>36</sup> 265.3, 248.9 and 270.4 kcal mol<sup>-1</sup>, respectively, reflect their differing basicities and confirm that an *ortho*-carboranyl group is more strongly e-withdrawing than perfluorophenyl. Replacing both Ph groups in **I** with <sup>t</sup>Bu groups has the opposite effect, with  $^1J_{\text{PSe}}$  of **VIIISe** measured as 777 Hz, as expected since <sup>t</sup>Bu is a classic electron-donating group. **VIII**, [1-<sup>t</sup>P'Bu<sub>2</sub>-*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ], is calculated to be the strongest of the C-bound carboranylphosphine bases in this study [PA(**VIII**) = 274.0 kcal mol<sup>-1</sup>]. Note that the analogous <sup>i</sup>Pr species [1-P(Se)(<sup>i</sup>Pr)<sub>2</sub>-*closo*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ ] has been reported but no  $^1J_{\text{PSe}}$  given.<sup>7</sup> For this, the calculated PA is 273.5 kcal mol<sup>-1</sup>, in line with a slightly less electron-rich alkyl substituent. The reduction in  $^1J_{\text{PSe}}$  from **ISe** to **VIIISe** is partially recovered in **3Se** ( $^1J_{\text{PSe}}$  = 792 Hz, PA = 262.6 kcal mol<sup>-1</sup>) in which one <sup>t</sup>Bu is replaced by the more electron-poor H. Analogs of **3Se** with <sup>t</sup>Bu replaced by <sup>i</sup>Pr and Cy are known and have similar  $^1J_{\text{PSe}}$  values [799 and 805 Hz, respectively, along with PA = 260.7 (<sup>i</sup>Pr) and 259.6 (Cy) kcal mol<sup>-1</sup>].<sup>31</sup>

An interesting comparison is that of the  $^1J_{\text{PSe}}$  values of **4Se** (where the carborane cages are not linked) and **XISe** [cages linked; a phosphine selenide based on 1,1'-bis(*ortho*-carborane)],<sup>8</sup> 846 and 891 Hz respectively. This implies that phosphine **XI** is a weaker base than phosphine **4**, i.e. simply connecting the two carborane cages significantly reduces the carboranylphosphine basicity as measured by  $^1J_{\text{PSe}}$ . This can be traced to a rehybridisation of the P atomic orbitals on cage-linking. Although the structure of **4** has not been determined (the compound is an oil) that of the  $\text{C}_{\text{cage}}\text{Me}$  analog **XII** is known<sup>23</sup> and serves as an appropriate substitute (confirmed by the close similarity of the calculated PAs of **4** and **XII**, 248.9 and 249.4 kcal mol<sup>-1</sup>, respectively). The structure of **XI** was published two years ago.<sup>8</sup> Figure 9 compares crystallographically-determined bond distances and interbond angles at the P centers in **XII** and **XI**. There is practically no difference in equivalent distances and the  $\text{C}_{\text{cage}}\text{--P--Ph}$  angles differ by no more than 4°. However, the  $\text{C}_{\text{cage}}\text{--P--C}_{\text{cage}}$  angle in **XI** is ca. 15° less than that in **XII**. This implies more P 3p character in the P- $\text{C}_{\text{cage}}$  bonds in **XI** and consequently more P 3s character in the P lone pair, consistent with **XI** being the weaker base. **XISe** has the largest  $^1J_{\text{PSe}}$  value of all the carboranylphosphines surveyed here. **XI** and its Et analog are the least-basic carboranylphosphines currently known.<sup>8</sup> In terms of their calculated PAs, **4** and **XI** appear more similar (PA = 248.9 and 248.8 kcal mol<sup>-1</sup>, with the corresponding gas phase data suggesting a greater difference, see SI for discussion). It is interesting to note that the linear relationship shown in Figure 8 under-estimates the  $^1J_{\text{PSe}}$  data for the former, while over-estimating it for the latter, highlighting limitations of this approach, as discussed further in the SI.



**Figure 9.** Distances (Å, black) and angles (°, red) around the P atoms in (left) **XII** and (right) **XI**, showing a significant narrowing of the  $\text{C}_{\text{cage}}\text{--P--C}_{\text{cage}}$  angle in the bis(carborane) cage.

### Changing the group on the second cage C atom

Here we compare two families of carboranylphosphine selenides, one based on *ortho*-carborane and the other on *meta*-carborane. Replacing H on C2 in **I** with the formally EDG Me to give **IV** and the formally EWG Ph to give **V** affords little variation in the  $^1J_{\text{PSe}}$  values of the corresponding selenides, 799, 804 and 812 Hz, respectively. A  $\text{PPh}_2$  unit attached to C2 also has little effect, with  $^1J_{\text{PSe}}$  for **VSe** being 807 Hz. Similarly, the calculated PA values of the phosphines **I**, **IV**, **V** and **VI** are little varied, all lying between 265 and 267 kcal mol $^{-1}$ .

A very similar conclusion is drawn from consideration of the *meta*-carborane family. Compounds **IISe**, **VIISe**, **1Se** and **2Se** show minimal change in recorded  $^1J_{\text{PSe}}$  values (797, 804, 802 and 802 Hz, respectively, also reflected in the PA data, Table 1) implying that the basicities of the parent carboranylphosphines are little different from each other, in spite of the fact that in **1** and **2** a strongly EWG (a C-bound carborane) is bonded to the reference cage at the C7 position.

In these two families of carboranylphosphines a carborane is a substituent to a  $\text{PPh}_2$  unit and the variation between members is in the substituent to that substituent. The evidence above appears to show that such second-order substitution has very little, if any, influence on the basicity of the  $\text{PPh}_2$  group.

### Changing the carborane isomer

It is well-known that carboranes generally exist in more than one isomeric form. Potentially the nature of the carborane isomer could influence the Lewis basicity of an appended phosphine but to date no study exploring this possibility has been reported. In **I**, **II** and **III** the  $\text{C}_2\text{B}_{10}\text{H}_{11}$  substituent to the  $\text{PPh}_2$  unit is present as, respectively, the 1,2- (*ortho*), 1,7- (*meta*) and 1,12- (*para*) isomer.  $^1J_{\text{PSe}}$  values for **ISe** and **IISe** are practically the same, 799 and 797 Hz, respectively, suggesting that both *ortho*- and *meta*-carborane have the same effect on the basicity of an appended  $\text{PPh}_2$  group. Although carboranylphosphine **III** is a known species<sup>13</sup> the high cost of [*closo*-1,12- $\text{C}_2\text{B}_{10}\text{H}_{12}$ ] prevented us from remaking it to subsequently synthesise the selenide **IIISe**. However, the close similarity of the calculated PAs for all three members of the family **I**, **II** and **III** (265–271 kcal mol $^{-1}$ ) suggests that the basicity of a carboranylphosphine is little altered by changing the isomeric form of the carborane. We have also calculated PAs of two currently unknown derivatives of **III**, [1- $\text{PPh}_2$ -12-Me-*closo*-1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ] (**XIII**, PA 270.7 kcal mol $^{-1}$ ) and [1- $\text{PPh}_2$ -12-Ph-*closo*-1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$ ] (**XIV**, PA 269.9 kcal mol $^{-1}$ ). See Chart 2. The close similarity of these PAs to the PA values of **IV** and **V** (265.0 and 266.6 kcal mol $^{-1}$ , respectively) further supports the conclusion that changing the carborane isomer has little effect, and their very close similarity to the PA of **III** (270.3 kcal mol $^{-1}$ ) reinforces the finding above that changing the substituent on the second carbon atom also has negligible effect.

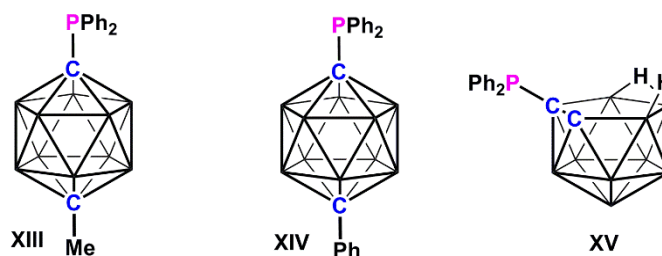


Chart 2. Currently unknown carboranylphosphines **XIII**, **XIV** and **XV**.

### C-bound vs. B-bound phosphine

Early studies by Hawthorne and co-workers,<sup>5a</sup> further developed by Teixidor, Viñas et al.<sup>5c</sup> and more recently by Spokoyny and colleagues<sup>5d,e</sup> have shown that, while a substituent attached to the C atom of a carborane generally experiences an electron-withdrawing effect,<sup>5b</sup> one attached to a B vertex distant from C experiences electron donation. In the context of carboranylphosphines, Spokoyny et al. compared the C-phosphino *meta*-carborane **II** with the B9-phosphino analog **IX** in terms of: (i) their ability to displace COD from [Pt(COD)Cl<sub>2</sub>]; (ii) the CO stretching frequency of the complex [*trans*-Rh(CO)(Cl)(phosphine)<sub>2</sub>]; and (iii) the calculated charges on the P atoms and the energies of the P lone pair of electrons.<sup>5e</sup> All of these studies concluded that the P atom in **IX** is significantly more electron-rich than that in **II**, i.e. that **IX** is more basic. Comparisons of the calculated PAs of these carboranylphosphines and the <sup>1</sup>J<sub>PSe</sub> values of their selenides fully support this conclusion. Thus **IISe** has <sup>1</sup>J<sub>PSe</sub> of 797 Hz compared to that of **IXSe** of 704 Hz,<sup>3</sup> while the PA for **IX** is ca. 10 kcal mol<sup>-1</sup> greater than that of **II** (280.3 vs. 269.0 kcal mol<sup>-1</sup>). The B9-substituted phosphine **IX** is the most basic of all the carboranylphosphines considered in this work. Note, however, that *P*-alkyl analogs of **IX** appear, not surprisingly, to be somewhat more basic.<sup>5e</sup>

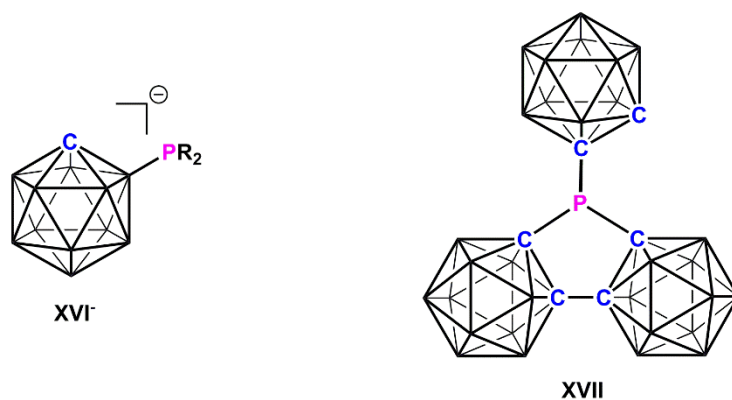
### Closo vs. nido carborane

Of all the selenides considered in this study the anionic nido species **XSe<sup>-</sup>** has the second lowest <sup>1</sup>J<sub>PSe</sub> value, 737 Hz [PA (**X<sup>-</sup>**) = 279.9 kcal mol<sup>-1</sup>], consistent with the carboranylphosphine **X<sup>-</sup>** being strongly basic. However, since **X<sup>-</sup>** is the first nido carboranylphosphine to be reported it is instructive to consider whether its high basicity is due to it being nido or anionic (or perhaps both).

The matter is readily resolved by a further PA calculation on the currently-unknown analogous neutral nido carboranylphosphine **XV** (Chart 2), affording PA = 269.6 kcal mol<sup>-1</sup>, fully in line with that of the parent closo carboranylphosphine **I**, implying that the high basicity of **X<sup>-</sup>** is predominantly due to the fact that it is anionic. This is fully consistent with a recent study by Lavallo and co-workers who have demonstrated that the C-functionalised anion [*closo*-1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> is a much stronger electron donor than the C-functionalised neutral carborane [*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>].<sup>37</sup>

## ■ CONCLUSIONS

This study has investigated, both experimentally and computationally, a number of factors that influence the basicity of carboranylphosphines. As anticipated, significant changes in basicity arise from changing the nature of the other groups directly attached to P, as has been demonstrated many times for phosphines generally. With specific reference to carboranylphosphines, however, further significant modifications to basicity arise from the charge on the carborane cage and the nature of the cage vertex to which the P atom is attached. In contrast, the isomeric nature and/or the positioning of substituents on the carborane cage appear to have minimal influence on phosphine basicity. Carboranylphosphine basicity can be *maximised* by attaching the P atom to a B atom distant from the C vertices of the carborane and by the cage carrying a negative charge. Thus the currently unknown species [*closo*-2-PR<sub>2</sub>-1-CB<sub>11</sub>H<sub>11</sub>]<sup>-</sup> (**XVI<sup>-</sup>**) (Chart 3) and its 7-PR<sub>2</sub> and 12-PR<sub>2</sub> isomers would be predicted to be very strongly basic [PA (**XVI<sup>-</sup>**) = 285.4 kcal mol<sup>-1</sup>]. On the other hand carboranylphosphine basicity can be *minimised* by maximising the number of C-bound carborane cages and arranging for two of these to be linked. Accordingly, the unique species [μ-2,2'-{P(1''-*closo*-1'',2''-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)}-(1-(1'-*closo*-1',2'-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)-*closo*-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)] (**XVII**), also currently unknown, is expected to be an exceptionally weak base, fully consistent with an extremely low calculated PA of 234.4 kcal mol<sup>-1</sup>. Between these extremes a vast number of carboranylphosphines of differing basicities can be envisaged. Given the ubiquitous nature of phosphines in both transition-metal and metal-free catalysis, this exceptional tuneability in basicity is likely to be important in future applications of carboranylphosphines.



**Chart 3.** The unknown carboranylphosphines **XVI<sup>-</sup>** and **XVII**. Based on the conclusions of this study **XVI<sup>-</sup>** is predicted to be strongly basic, while **XVII** is predicted to be very weakly basic.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.xxxxxxx. This information comprises crystallographic data, NMR spectra of all new compounds, computational details and related references, calculated data, as well as xyz coordinates of all geometry-optimized models.

### Accession Codes

CCDC 1946353-1946362 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

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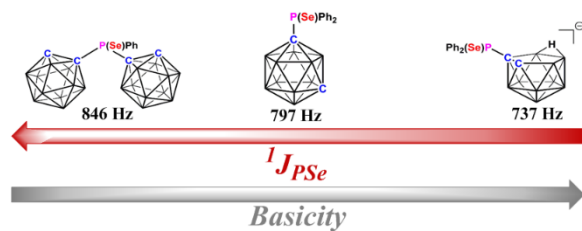
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The relative basicities of a range of carboranylphosphines are assessed by consideration of the  $^1J_{PSe}$  NMR coupling constants of their selenides and calculated proton affinities, which are essentially inversely correlated. The various factors which significantly influence carboranylphosphine basicity are thereby identified.